京都電子工業株式会社
KYOTO ELECTRONICS MANUFACTURING CO.,LTD.

Application Note

Determination of dissolved oxygen in water

Industry	Chemical
Instrument	Automatic potentiometric titrator
Measurement method	Potentiometric titration / Redox Titration
Standards	JIS K 0102

1. Scope

Iodometry is stipulated in JIS K 0102 Testing methods for industrial wastewater as a method for quantifying dissolved oxygen. Only manual titration is stipulated in the standard. However, the same method can be achieved using an automatic potentiometric titrator. An overview of the iodometry is described below.
When a manganese sulfate solution and a sodium hydroxide solution are added to a sample, a white precipitate of manganese (II) hydroxide is formed.

$$Mn_2^+ + 2OH^- \rightarrow Mn(OH)_2$$

This manganese (II) hydroxide is oxidized by the dissolved oxygen in the water, forming a brown precipitate.

$$Mn(OH)_2 + 1/2O_2 \rightarrow MnO(OH)_2$$

When the brown precipitate is dissolved in the presence of iodide ions, an amount of iodine is released, corresponding to the amount of dissolved oxygen.

$$MnO(OH)_2 + 2I^- + 4H^+ \rightarrow Mn_2^+ + I_2 + 3H_2O$$

The amount of dissolved oxygen is determined by titrating the iodine released with a sodium thiosulfate solution.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

2. Precautions

To prevent leakage and changes of the electrolyte concentration when storing the electrode, seal the electrolyte filling port in the electrode with a rubber stopper.

3. Apparatus

Main unit	Automatic potentiometric titrator (preamplifier : STD)
Electrode	Combined platinum electrode (Inner filling (outer) 3.3 mol/L potassium chloride solution)

4. Reagents

- 0.025 mol/L Sodium thiosulfate solution
- Manganese sulfate solution
  Solution dissolved with 240 g of the manganese(II) sulfate pentahydrate in pure water and then diluted it with pure water up to 500 mL.
- Alkaline potassium iodide - sodium azide solution
  Solution dissolved with 350 g of sodium hydroxide, 75 g of potassium iodide, and 10 g of sodium azide in pure water, and then diluted it with pure water up to 500 mL.

・ Sulfuric acid
・ 10 g/L starch solution (used for manual analysis)

5. Procedure

1) Introduce the sample to a dissolved oxygen measurement bottle.
2) Insert the tip of a pipette into the water. Quickly add 1 mL of the manganese sulfate solution and 1 mL of the alkaline potassium iodide - sodium azide solution, respectively. Seal the bottle so that air does not mix with the solution.

3) Invert the bottle repeatedly for approximately 1 minute to diffuse the precipitate formed throughout the bottle.
4) Let the bottle stand so that the precipitate settles. Repeat step 3) and then let the bottle stand.
5) When the precipitate has settled and about 1/2 of the total is supernatant, remove the stopper. Add 1 mL of sulfuric acid, and then reseal the bottle.

6) Invert the bottle several times to dissolve the precipitate.
7) Transfer all of the solution in the bottle to another beaker.
8) Rinse the inside walls of the bottle with pure water, and transfer the rinse water to the beaker. Repeat this five or six times.

9) Titrate with 0.025 mol/L sodium thiosulfate, and identify the inflection point in the titration curve as the end point.

(For manual analysis, add 1 mL of the starch solution as an indicator after the solution becomes pale yellow, and titrate until the blue color disappears.).

6. Calculation

Dissolved oxygen (mg/L) = EP1 × TF × C1/S

EP1	Titration volume required to reach the first end point (mL)
TF	Factor of titrant (0.9910)
C1	Concentration conversion coefficient (200)
S	Amount of sample introduced (mL)

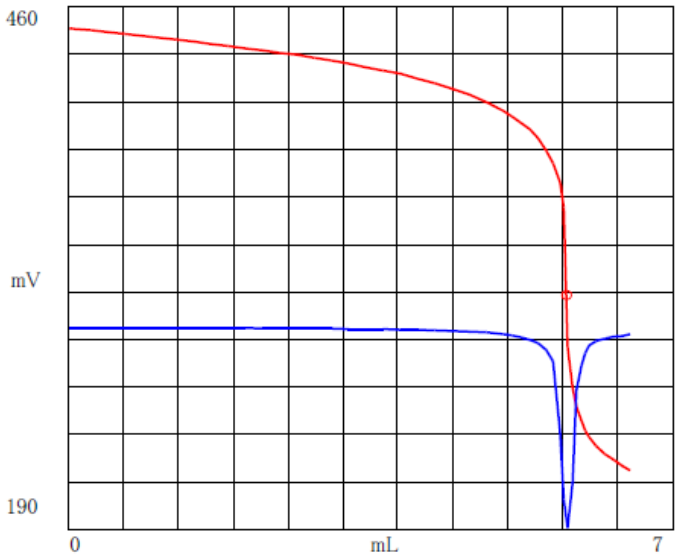
7. Example

— Parameter —

＜Titr. Mode＞	Auto Intermit	**＜Ctrl. Para.＞**	
＜Titr. Form＞	EP Stop	Number of EP	1
		End Sense	Auto
＜Titr. Para.＞		Gain	1
Max. Volume	20 (mL)	Data Sampling	Auto
Channel/Unit(Ctrl.)	Ch1, mV	Ctrl. Speed	Standard
Channel/Unit(Ref.)	Off	Other Ctrl.	Standard
pH Polarity	Standard	Auto Int. Mode	Standard
Titr. Type Check	No Check	Stirrer Speed	4
Dose Mode	None		

（The above condition is an example. The setting condition depends on the model.）

— Example of Titration curve —



— Measurement results —

Table 1 Measurement result by potentiometric titration method

	Sample (g)	Titration (mL)	Dissolved oxygen (mg/L)
1	139.95	5.7817	8.19
2	139.95	5.7655	8.16
3	139.95	5.7814	8.19
Average			8.18
SD			0.02
RSD (%)			0.24

Table 2 Measurement result by manual titration method

	Sample (g)	Titration (mL)	Dissolved oxygen (mg/L)
1	133.73	5.50	8.15
2	133.73	5.50	8.15
3	133.73	5.49	8.14
Average			8.15
SD			0.01
RSD (%)			0.12

8. Summary

Comparable measurement values were obtained using an automatic potentiometric titrator. With the potentiometric titration, there is no need to add an indicator, and individual differences in endpoint determination by different analysts can be eliminated.